

REQUEST FOR RECONSIDERATION

Claims 1-11 remain active in this application.

The claimed invention is directed to a process for free-radical polymerization in the presence of a regulator.

Applicant wishes to thank Examiner Bernshteyn and Supervisory Patent Examiner Wu for the helpful and courteous discussion held with their U.S. representative on July 27, 2006. At that time, Applicant's U.S. representative argued that Baguley et al. fail to describe free radical **polymerization** and that the Ziegler-Natta polymerization catalyst used in Takeshi also fail to describe **free radical** polymerization. The following is intended to expand upon the discussion with the Examiner.

Polymerization processes are sometimes conducted in the presence of regulators which can reduce the formation of an insoluble gel fraction. While many sulfur containing regulators are known and used, they typically have the disadvantage of a malodor and can be irritating to the skin, disadvantages which are particularly severe for use in cosmetic applications. Accordingly, regulators which avoid these problems are sought.

The claimed invention addresses this problem by providing a method for free radical polymerization in the presence of a regulator in which certain carbocyclic or heterocyclic regulator compounds are used. Applicant has discovered that such carbocyclic and heterocyclic compounds are effective regulators for a free-radical polymerization process. Such a process is nowhere disclosed or suggested in the cited prior art of record.

The rejection of claims 1-4 and 7-11 under 35 U.S.C. §102(b) over Ishihara et al., JP7-090012 is respectfully traversed.

Ishihara et al. fail to disclose or suggest a free radical polymerization process. Ishihara et al. describes a solid catalyst containing a metal oxide preferably SiO₂, Mg, Ti, a halogen and an electron-donative compound such as di-n-butyl phthalate (see Abstract)

which is used in a polymerization process of propylene. The solid catalyst is a Ziegler-Natta type polymerization catalyst which functions by the insertion of the monomer between the metal and the growing chain, a process which is not recognized by those of skill in the art as a free-radical polymerization process. As evidence of the distinction between free radical polymerization and polymerization in the presence of a Ziegler-Natta catalyst, Applicant encloses herewith a passage from *Morrison & Boyd Organic Chemistry*, 6th Edition which on page 1087 identifies coordination polymerization as a revolutionary type of polymerization distinct from free-radical type polymerization using a catalyst discovered by Ziegler and Natta. Thus, those of skill in the art recognize that such a solid phase polymerization is not a free radical polymerization and accordingly Ishihara et al. fails to disclose or suggest a method of free-radical polymerization.

In contrast, the claimed invention is directed to a free radical polymerization process in the presence of a molecular weight regulator. As the reference fails to disclose or suggest a free radical polymerization process and applicant has demonstrated the art recognized distinction between a free-radical process and a polymerization process in the presence of a Ziegler-Natta catalyst, the claimed invention is clearly neither anticipated nor rendered obvious from this reference and accordingly withdrawal of the rejections under 35 U.S.C. §102(b) is respectfully requested.

The rejection of claims 1, 5-7 and 10 under 35 U.S.C. §102(b) over Baguley et al. is respectfully traversed.

Baguley et al. fails to disclose or suggest a method of free-radical polymerization.

Baguley et al. merely describes free-radical alkylation and cyclizations which are mediated by carbocyclic mediators. The reference fails to disclose or suggest a free-radical **polymerization** process.

In contrast, the claimed invention is directed to a free-radical polymerization process in the presence of a carbocyclic or heterocyclic compound as a regulator. As the reference fails to disclose or suggest a method of free-radical polymerization, the claimed invention is clearly neither anticipated nor rendered obvious and accordingly withdrawal of the rejection under 35 U.S.C. §102(b) is respectfully.

Applicant submits this application is now in condition for allowance and early notification of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.
Norman F. Oblon



Richard L. Chinn, Ph.D.
Registration No. 34,305

Customer Number
22850

Tel: (703) 413-3000
Fax: (703) 413 -2220
(OSMMN 03/06)
RLC/rac

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Prefa
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SEC. 31.6

COORDINATION POLYMERIZATION

1087

Problem 31.6 Draw the structure of the product expected from the killing of living polystyrene by each of the following reagents: (a) water; (b) carbon dioxide, then water; (c) small amount of ethylene oxide, then water; (d) a large amount of ethylene oxide, then water.

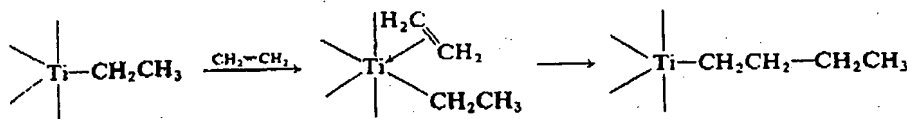
3.6 Coordination polymerization

Until 1953, almost all vinyl polymerization of commercial importance was of the free-radical type. Since that time, however, a new kind of polymerization, coordination polymerization, has revolutionized the field. Following discoveries by Karl Ziegler (Max Planck Institute for Coal Research) and by Giulio Natta (Polytechnic Institute of Milan)—who jointly received the Nobel Prize in 1963 for this work—catalysts have been developed that permit control of the polymerization process to a degree never before possible.

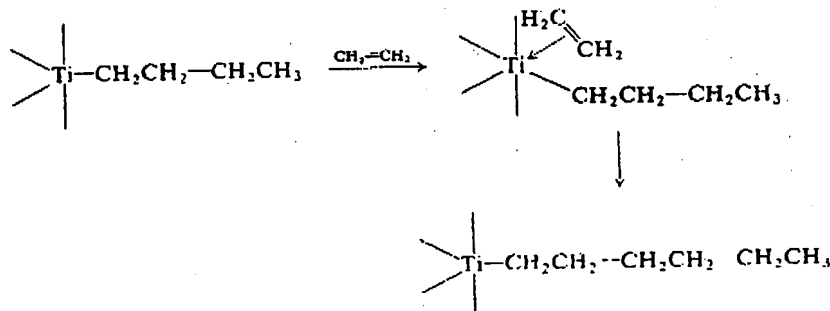
In Chapter 29 we saw examples of the remarkable power of transition metal complexes to bring about and control organic reactions. Here, in these polymerization catalysts, we see another.

Ziegler-Natta catalysts are made up of a transition metal salt—typically titanium trichloride—and a metal alkyl like triethylaluminum. These react to form the active catalyst: a titanium complex holding an ethyl group.

Now the alkene—ethylene, say—is introduced. According to the generally accepted mechanism, the alkene attaches itself to titanium by a π bond: the π cloud of the alkene overlaps an empty orbital of the metal (Sec. 29.5). Next, with



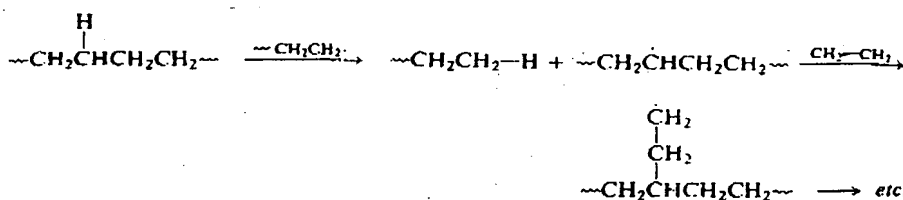
ethyl and the alkene both held by the metal, the first of many similar steps takes place. The ethylene unit *inserts itself between metal and the ethyl group*. In place of ethyl there is now a *n*-butyl group attached to titanium. The bonding site where ethylene was held is vacant again, and the catalyst is ready to work again. Another ethylene becomes π bonded to the metal, and then inserts itself between the metal and alkyl to form, this time, a *n*-hexyl group. And so the process continues over and over again, with the alkyl group growing by two carbons in each cycle. Finally, perhaps through the insertion of hydrogen, the long chain separates from the metal and a molecule of polyethylene has been formed.



We see here another example of *symphoria*—the bringing together of molecules for a useful purpose. The basic similarity of this mechanism to the ones for homogeneous hydrogenation (Secs. 29.5–29.7) and the oxo process (Sec. 29.8) is striking. Titanium holds an alkyl group where rhodium or cobalt held hydrogen. In each case there is a vacant bonding site—an empty orbital—on the metal, through which the alkene can become π bonded before it inserts itself into a bond: between titanium and alkyl, between rhodium and hydrogen, or between cobalt and hydrogen. Here, as in those other reactions, the net process is *addition*: the insertion amounts to the addition of metal and alkyl across the double bond.

Polymerization with Ziegler–Natta catalysts has two important advantages over free-radical polymerization: (a) it gives *linear* polymer molecules; and (b) it permits *stereochemical control*.

Polyethylene made by the free-radical process has highly branched chains due to chain transfer of a special kind, in which the chain-transfer agent is a *polymer molecule*. At the high temperatures required for this particular polymerization, the growing free radicals not only *add* to the double bond of a monomer but also *abstract* hydrogen from a chain already formed. This abstraction generates a free-radical center from which a branch can now grow. These highly branched polyethylene molecules fit together poorly and in a random way; the compound is said to have low *crystallinity*. It has a low melting point and is mechanically weak.



In contrast, polyethylene made by the coordination process is virtually unbranched. These unbranched molecules fit together well, and the polymer has a high degree of crystallinity. It has a higher melting point and higher density than the older (*low density*) polyethylene, and is mechanically much stronger. (We shall look at the crystallinity of polymers and its effect on their properties in Sec. 31.8.)

A second, far-reaching development in coordination polymerization is *stereochemical control*. Propylene, for example, could polymerize to any of three different arrangements (Fig. 31.1): *isotactic*, with all methyl groups on one side of an extended chain; *syndiotactic*, with methyl groups alternating regularly from side to side; and *atactic*, with methyl groups distributed at random.

By proper choice of experimental conditions—catalyst, temperature, solvent—each of these stereoisomeric polymers has been made. Atactic polypropylene is a soft, elastic, rubbery material. Both isotactic and syndiotactic polypropylenes are highly crystalline: regularity of structure permits their molecules to fit together well. Over three billion pounds of isotactic polypropylene is produced every year, to be molded or extruded as sheets, pipes, and filaments; it is one of the principal synthetic fibers.

Coordination catalysts also permit stereochemical control about the carbon–carbon double bond. By their use, isoprene has been polymerized to a material virtually identical with natural rubber: *cis*-1,4-polyisoprene. (See Sec. 11.24.) This, like formation of isotactic polypropylene—and like hydrogenation with Wilkinson's catalyst—we recognize as an example of stereoselective synthesis (Sec. 10.2).

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